DEP .TION OF COPPER AND NICKEL FROM DI!UTE SOLUTIONS IN PACKED BED ELECTROLYTIC CELLS

A thesis submitted to the Faculty of Engineering, University of the Witwatersrand, in fulfilment of the requirements for the degree of Doctor of Philosophy

by
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DECLARATION

The thesis entitled
"Deposition of Copper and Nickel from Dilute Solutions in Packed Bed Electrolytic Cells"
is the result of my own unaided work, except where specifically stated in the acknowledgements. No part of this thesis has been submitted, or is being submitted, to any other University for any reason whatsoever. This thesis is an extension of a dissertation submitted to the University of the Witwatersrand in October 1978, in which the main experimental and theoretical results were first presented. All work reported in this thesis was performed while at the University of the Witwatersrand.

1st April, 1981

K.A. Dardis

SYNOPSIS

A number of investigations have been conducted into the removal of metals from dilute solutions in packed bed electrochemical reactors and the feasibility of this tecnnique has been demonstrated for the removal of metal ions more noble than the hydrogen ion. Very little information is, however, available for the treatment of less noble metals, for which the competing process of hydrogen evolution is likely to prove particularly troublesome and which might greatly reduce the efficiency of the metal removal.

A one-dimensional mathematical model for the packed bed electrode is developed and is tested on experimental results for the removal of copper and nickel from dilute solution. It is shown that for engineering purposes the model can be applied to the two-dimensional flow-by electrode configuration, which is better suited to practical application and scale-up than the often studied, but rather impractical, one-dimensional flow-through electrode. The engineering model is based on published theory and is applicable to porous electrodes in which multiple electrode reactions take place. Consideration is given to the potential profiles developed within the electrode and to the electrochemical kinetics of the cell reactions. Mass transfer limitations on the kinetics are also included in the treatment.

In this investigation novel methods for the analytical and numerical solution of the packed bed electrode equation are developed. The numerical solution is applied to the calculation of electrochemical kinetic parameters which best fit the predictions of the model to the results of the experimental investigations.

The results of an earlier investigation into copper removal are used to test the predictions of the mathematical model in the case of a metal more noble than the hydrogen ion. No suitable results were available for less noble metals and an experimental investigation was therefore conducted into the electrochemical removal of nickel ions from dilute solution in an electrolytic cell with a flow-by packed bed cathode. In order that the experimental results might be directly applicable to the conditions encountered in the treatment of dilute effluents no additional supporting electrolyte, other than small quantities of sulphuric acid,

was added to the solution. The effects on the nickel removal efficiency of the nickel concentration, electrode current, catholyte flowrate and catholyte pH were investigated. Nickel concentrations of less than one part per million were obtained at acceptable current efficiencies from solutions having starting concentrations of approximately one hundred parts per million.

Good correspondence is obtained between the experimental and theoretical results for both nickel and copper removal. The fitted values of the electrochemical kinetic parameters for copper removal are in very good agreement with values reported in the literature. The best fit of the nickel results, on the other hand, is obtained with a value for the Tafel slope for the side reaction which is far different from reported literature values appropriate to the simple side reaction process of hydrogen evolution.

It is shown by means of independent experiments at a rotating disc electrode that oxygen, present as a dissolved impurity in the experimental solution, takes part in additional side reactions. The complex side reaction processes may nevertheless be lumped into a single overall side reaction, which may be described with an adequate degree of engineering accuracy over the range of experimental conditions of this investigation by Tafel-type electrochemical kinetics. The range of the experimentally determined apparant kinetic parameters for the overall side reaction determined at the rotating disc electrode brackets the values fitted to the model, thus further confirming the engineering validity of the mathematical model, as already demonstrated by the accuracy of the model fit to the results for copper removal. The results of this investigation clearly underline the need for the incorporation of experimentally determined electrochemical kinetic parameters into the design of industrial electrochemical reactors, for which impurity effects may be significant, in preference to literature values determined in ultrapure solutions.

The performance of a complete system, incorporating a packed bed electrochemical reactor through which a dilute solution of nickel sulphate is continuously recirculated, is also examined. The predictions of a simple model agree well with actual experimental results and illustrate how the one dimensional model for multiple reactions in a porous electrode may be applied to the design of systems for metal removal.

A scaled-up industrial pilot unit was designed on the basis of the engineering model and results are reported for the treatment of a mixed effluent from an electroplating works.

To Sue, my wife,for her understanding
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NOMENCLATURE

A	Area of current feeder = membrane area. (cm^2)
a	Specific interfacial area, (cm^{-1})
a	Constant in Tafel equation [2.16]. (volts)
a_i	Activity of species i
B	Constant in porous electrode equation written for dimensionless length, $B = L^2 b$. (ohms cm^2)
b	Constant in porous electrode equation, $b = a\left(\frac{1}{\kappa} + \frac{1}{\sigma}\right)$. (ohms)
b	Tafel slope in Tafel equation [2.16]. (volts)
C	Concentration. (ppm)
C_D	Double layer capacity.
C_d	Capacity of the diffuse double layer.
$\mathfrak{C}$	Concentration in molar units. (moles/cm^3 or moles/ℓ)
$\bar{\mathfrak{C}}$	Mean concentration of flowing solution or Bulk concentration.
$\mathfrak{C}_{N,O}\mathfrak{C}_{H,O}$	Concentrations of nickel and hydrogen ions at the cell inlet. (moles/l)
$\mathfrak{C}_{N,1}$ $\mathfrak{C}_{H,1}$	Concentrations of nickel and hydrogen ions at the cell outlet. (moles/l)
D	Diffusion coefficient. (cm^2/sec)
D_p	Equivalent average particle diameter. (cm)
d	Membrane thickness. (cm)
E	Potential. (volts)
E^o	Standard electrode potential. (volts)
e	Electronic charge.
F	Faradays constant. (96487 coulombs/equivalent)
f(n)	Function defined by equation [B.25].
G	Superficial mass flowrate. (g/cm^2 sec)
G(X)	Function defined by $G(X) = Po^2 + 2B\,[\psi(n)-\psi(n_1)]$
I	Current. (A)
I_{ij}	Partial current for production of species i in reaction j. (A)
i	Superficial current density. (A/cm^2)
i_o	Exchange current density. (A/cm^2)

i_{oj}	Exchange current density for reaction j. (A/cm^2)
$i_{oj,ref}$	Exchange current density for reaction j at a reference concentration $C_{i,ref.}$ (A/cm^2)
i_d	Limiting current density. (A/cm^2)
i_{nj}	Transfer current for reaction j per unit interfacial area. (A/cm^2)
i_1	Superficial current density in the matrix phase. (A/cm^2)
i_2	Superficial current density in the solution phase. (A/cm^2)
i_+	Anodic partial current density. (A/cm^2)
i_-	Cathodic partial current density. (A/cm^2)
J	Flux. (moles/cm^2 sec)
J_d	Mass transfer factor, $Jd = k_m Sc^{2/3}/v_y$.
Jin	Pore wall flux of species i. (moles/cm^2 sec)
k_m	Mass transfer coefficient. (cm/sec)
k_L	Mass transfer parameter in the porous electrode equation, defined by equation [2.38]. (coul cm/mole sec)
k_1	Kinetic parameter for the main reaction in the porous electrode equation, defined by equation [2.36]. (A/cm^2)
k_2	Kinetic parameter for the side reaction in the porous electrode equation, defined by equation [2.37]. (A/cm^2)
L or L_x	Electrode length in the direction of current flow. (cm)
L_y	Electrode length in the direction of electrolyte flow. (cm)
M_i	Symbol for the chemical formula of species i.
N_i	Flux of i. (moles/cm^2 sec)
N_H	Hydrogen ion back migration rate. (moles/sec)
N_j	Quantity of i produced by j cell reactions. (moles)
N_{ij}	Quantity of i produced in cell reaction j. (moles)
n	Electrode reaction valence.
P	Variable defined by $P = dn/dX$.
Q	Flowrate. (l/min)
q_{ij}	Cathodic reaction order
R	Universal gas constant (J/mole K)

Re	Particle Reynolds Number, $Re=D_p G/\mu$.
S_{ij}	Stoichiometric coefficient of species i in reaction j.
Sc	Schmidt number, $Sc=\mu/\rho D$.
T	Absolute temperature. (K)
t	Time. (secs)
U°_j	Standard electrode potential for reaction j. (volts)
U°_r	Standard electrode potential of reference electrode. (volts)
U_{jw}	Open circuit potential for reaction j at the local wall concentration relative to a reference electrode of a given kind.
ΔU	$\Delta U=U_S-U_R$, the difference between the open circuit potentials of the side reaction and main reaction at chosen reference concentrations. (volts)
u	Ionic mobility. (cm^2mole/J sec)
V	Volume. (ℓ)
v	Volume. (cm^3)
v_x	Electrolyte velocity in the direction of current flow. (cm/sec)
v_y	Electrolyte velocity in the direction of solution flow. (cm/sec)
x	Length co-ordinate.
X	Dimensionless length, X=x/L.
y_1, y_2	Variables defined by equation [3.31].
z	Charge transfer valence in the Butler-Volmer equation.
z_i	Charge number of species i.
z_R	Valency of a substance in solution which complexes with metal ions in solution.
$z_{o,i}$	Electrochemical reaction order of species i.

Greek Letters

α	Transfer coefficient.
α_{aj}	Anodic transfer coefficient for reaction j.
α_{cj}	Cathodic transfer coefficient for reaction j.
α^*	Effective transfer coefficient in the Butler-Volmer equation for weakly supported electrolytes, equation [2.21].
β_1	Kinetic parameter for the main reaction in the porous electrode equation, defined by equation [2.39]. ($volts^{-1}$)

β_2 Kinetic parameter for the side reaction in the porous electrode equation, defined by equation [2.40]. (volts^{-1})

γ_{ij} Exponent in the equation for the composition dependence of the exchange current density, defined by equation [B.16].

δ Diffusion layer thickness. (cm)

ε Packed bed void fraction.

ε_1 Small dimensionless distance.

ζ Zeta potential. (volts)

ζ_0 Zeta potential at the equilibrium potential, E°. (volts)

η Overpotential. (volts)

η Local overpotential, $\phi_1-\phi_2$. (volts)

η_t Charge transfer overpotential. (volts)

η_R Reaction overpotential. (volts)

η_c Crystallisation overpotential. (volts)

η_d Diffusion overpotential.(volts)

η_{sj} Surface overpotential for reaction j, defined by $\eta_{sj}=\phi_1-\phi_2-U_{jw}$. (volts)

η_0 or η_o Local overpotential measured at the free solution interface of the packed bed electrode. (volts)

η_1 Local overpotential measured at the current feeder. (volts)

η^* Local overpotential within the packed bed electrode at the point $X=1-\varepsilon_1$. (volts)

κ_0 Specific conductivity of the solution phase. (mho/cm)

κ Effective specific conductivity of the solution phase. (mho/cm)

λ Ionic equivalent conductance. (mho/cm^{2}equiv)

μ Viscosity. (g/cm sec)

ν_{ij} Stoichiometric coefficient of component i in reaction j.

ξ_i Current efficiency for the production or consumption of species i.

ρ Density. (g/cm^3)

ρ_0 Density. (kg/cm^3)

σ_0 Specific conductivity of the matrix phase.(mho/cm)

σ Effective specific conductivity of the matrix phase. (mho/cm)

ϕ Potential. (volts)

ϕ_1 Electrostatic potential in the matrix phase. (volts)

ϕ_2 Quasi-electrostatic potential in the solution phase. (volts)

ϕ_s Shape factor for non-spherical particles.

$\psi(\eta)$ Function defined by equation [B.30].

ω Angular velocity (radians/sec)

Subscripts

eq	Equilibrium.
N	Nickel.
H	Hydrogen ion.
C	Copper.
i	Species i.
j	Reaction j.
OX	Oxidised species.
RED	Reduced species.
R	Reactant in main reaction.
S	Reactant in side reaction.
ref	Denotes reference conditions.
w	Denotes conditions at pore wall.
r	Refers to reference electrode compartment.

1 INTRODUCTION

1.1 Heavy Metal Pollution - the Background to the Problem

The harmful effects of heavy metals on human and animal life have been known for a very long time : for instance, lead poisoning was probably first recognised by Hippocrates (370 BC) and mercurialism was described in AD 29 by Pliny in his writings on the diseases of slaves (1).

It is only in recent years, however, that public concern, spurred by such incidents as outbreaks since the early 1950's of minamata disease (the deformation of the foetus in the womb due to mercury absorbed by the mother), has led to the introduction of strict legislative standards governing exposure to heavy metals and the discharge of effluents containing these metals.

Such effluents are produced by a broad spectrum of sources which include the metal refining, metal plating, tanning, chlor-alkali, anodising and automotive industries. The wastes contain a wide range of metal ions including arsenic, antimony, cadmium, chromium, copper, lead, manganese, mercury, silver, selenuim and zinc. Electroplating effluents can also contain additional quantities of extremely toxic cyanide compounds. The magnitude of the problem may be gauged by the fact that it is estimated that at least 10 000 tons of copper are discarded in electroplating rinse waters in the U.K. annually (2) and in the United States the value of nickel and chromium lost in plating wastes has been conservatively estimated at 50-60 million dollars per year (3). In 1973 losses of chromium and nickel in the Johannesburg municipal area alone were estimated to cost a quarter of a million rands (4).

Toxic effects have been observed at very low intake levels and a representitive set of figures is given in Table 1.1(4,5). This toxicity poses further problems during the treatment in conventional sewage works of effluents containing these metals since, above certain threshold concentrations given in Table 1.2 (5), the metals can

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